

PATENT ABSTRACTS OF JAPAN

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(54) RELEASE FILM AND PROTECTIVE FILM FOR PREPREG USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a release film having both of high-degree dimensional stability and adhesion and a protective film for a prepreg.

SOLUTION: The release film is constituted by forming a release layer consisting of 15-85 weight % of a cellulosic resin and 85-15 weight % of a curable resin on one surface of a polyester film. The absolute value of the dimensional change ratio of this release film at a time when the release film is heated and cooled within a temperature range from ordinary temperature to 170°C under a stress of 0.785 MPa satisfies the formula: $(l_c - l_h)/l_h \leq 0.006$ (wherein l_c is a dimension at 30°C at a time of cooling and l_h is a dimension at 30°C at a time of heating) in the molding direction of the polyester film and the lateral direction vertical thereto.

$$\left| \frac{l_c - l_h}{l_h} \right| \leq 0.006$$

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CLAIMS

[Claim(s)]

[Claim 1] Consist of fibrin system resin and hardenability resin, and the mold releasing layer which contains 15 - 85 % of the weight and the latter 85 to 15% of the weight the former It is the ** form film formed in one field of polyester film. The ** form film with which the absolute value of the rate of a dimensional change at the time of carrying out heating cooling in 170 degrees C is characterized by being satisfied with the shaping direction of polyester film, and a cross direction vertical to it of the following formulas, respectively from ordinary temperature under the stress of 0.785MPa(s).

[Equation 1]

$$\left| \frac{l_c - l_h}{l_h} \right| \leq 0.006$$

Here, a dimension [in / in lc in the above-mentioned formula / 30 degrees C at the time of cooling] and lh show the dimension in 30 degrees C at the time of heating.

[Claim 2] The ** form film according to claim 1 which there is a coloring layer which consists of organic resin which contains a coloring agent in the field of another side of polyester film, and whose total light transmission of the whole ** form film is 25 - 75%, and has the permeability fluctuation when irradiating a beam of light with a wavelength [each] of 400-900nm in -5 - 5% of range.

[Claim 3] The ** form film according to claim 2 with which the organic resin which constitutes a coloring layer contains 15 - 85 % of the weight, and the latter for the former 85 to 15% of the weight by consisting of fibrin system resin and hardenability resin.

[Claim 4] A ** form film given in either of claims 1 or 3 which are at least one sort chosen from the group which fibrin system resin becomes from a cellulose nitrate, cellulose acetate, a sulfuric-acid cellulose, cellulose sodium xanthogenate, cellulose ester, methyl cellulose, ethyl cellulose, cellulose acetyl butyrate, cellulose acetyl propionate, a carboxymethyl cellulose, and hydroxyethyl cellulose.

[Claim 5] A ** form film given in either of claims 1 or 3 which are at least one sort of thermosetting resin chosen from the group which hardenability resin becomes from melamine resin, an epoxy resin, phenol resin, polyurethane resin, polyimide resin, an alkyd resin, a urea-resin, and acrylic resin.

[Claim 6] The ** form film according to claim 2 which is the black inorganic pigment which a coloring agent becomes from at least one sort of oxides chosen from the group which consists of Ti, V, Cr, Mn, Fe, Co, nickel, and Cu.

[Claim 7] The protection film for preregs characterized by using a ** form film according to claim 1 to 6.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the ** form film with which the heat dimensional stability in which a mold releasing layer contains fibrin system resin, and adhesion have been improved in more detail about a ** form film.

[0002]

[Description of the Prior Art] The ** form film has been used as carrier films for protection, such as carrier films for shaping, such as a binder coat, a resin sheet, a resin coat, or a ceramic green sheet, or prepreg. For example, after the vinyl-chloride-resin sheet used as a marking sheet carries out coating of the solution which melted vinyl chloride resin to the solvent on a ** form film (carrier film), it is obtained by carrying out heating clearance of the solvent, and the ** form film used in this way is called the carrier film for shaping. Moreover, the insulating resin sheet for the circuit boards (prepreg) carries out impregnation of the thermosetting resin to glass, paper, or a thermoplastic fiber textile, it is in the semi-hardening condition (B stage) which shows a solid property in ordinary temperature at the same time it evaporates a solvent etc., and carries out heating sticking by pressure with the metallic foil used as a circuit, and is made into a full hardening condition (C stage). In order to prevent that a foreign matter adheres on the surface of prepreg in the phase of a semi-hardening condition (B stage), or that other prepregs and blocking high occur in that case, a ** form film is made to rival on the surface of prepreg. And the ** form film used for the purpose of protection of a product front face in this way is called a protection film.

[0003] By the way, such a ** form film needs not to cause a dimensional change in the lamination ***** case. This is because a wrinkle and sag occur on a ** form film, exfoliation or a foreign matter will invade [a ** form film] from the part or irregularity called the wrinkle and sag will imprint on a protection front face, if a ** form film causes a dimensional change in the state of lamination *****. Especially this dimensional stability is strongly demanded with the protection film for prepregs which performs advanced heat-treatment of laser-beam-drilling processing etc. in the condition of sticking a ** form film.

[0004] As a means which raises dimensional stability, for example at least on one side of polyester film The resin layer which contains thermosetting resin or a photo-setting resin 70% of the weight or more The film tension concerning the ** form film at the time of forming so that it may become 3 - 20% on the basis of the thickness of the film obtained, and stiffening this resin layer by setting 400g /to 2 mm It is proposed by JP,11-277703,A that the heat-resistant film the rate of a heat shrink for 140 degree C and 5 minutes excelled [film] in the 0.13 - 0.18% of the die-length directions of a film and cross direction-0.06--0.11% dimensional stability can be obtained. Since surely according to this official report the resin layer which consists of the high thermosetting resin or the high photo-setting resin of dimensional stability to heat is arranged at the presentation and rate which can control a dimensional change and is moreover hardened under low tension, the heat-resistant film which has advanced dimensional stability is obtained.

[0005] however, when this invention persons inquire according to this official report, in using the heat-resistant film of this official report as a ** form film If the mold releasing layer which consists of hardenability silicone is formed and this is used as a surface-protection film of prepreg It was easy to exfoliate in the production process, and the silicon in a mold releasing layer shifted to the prepreg front face, and it found out that there was a fatal defect in which adhesion with next prepreg and a metallic foil becomes imperfection.

[0006] By the way, as for electronic parts, semi-conductor components, etc. which are used for those electronic equipment, small, and lightweight-izing and high integration are advancing in recent years with small [, such as electronic equipment especially mobile communication equipment represented by a cellular phone and the portable personal computer, and a Personal Digital Assistant device,] and lightweight-izing. Electronic parts, semi-conductor components, etc. which are used also about AV (audio-visual) device with new record media, such as DVC (digital video cassette) and DVD (digital videodisc), have the same demand. Various online test equipment is used into the production process of the resin sheet used as the component of the electronic parts used by these electronic equipment, or a substrate and semi-conductor components, or a ceramic sheet. With these test equipment, on a carrier film (a ** form film and a protection film are included) Positioning in circuit pattern printing, electrode printing, a laminating, a drilling process, etc., correction, etc. are made on detection of the fault of thickness spots and smoothness, such as a fabricated resin sheet, a pinhole, etc., and a pan. Usually, the sensor of these test equipment processes the information acquired from the laser light and the CCD camera (charge coupled device camera) of the thing using light, especially a light field, and is performing fault inspection and control of a location. In order that these test equipment may have detected the permeability and reflection factor of light which oscillated and emitted light with the standard light source or the fluorescent lamp called the light of specific wavelength like laser light or illuminant A, illuminant C, and D65 light source and may raise the detection sensitivity of these test equipment, combining a ** form film with the light of each test equipment, and coloring has been performed. However, some light of these test equipment of being unified into one was new, two or more sorts were used according to the object also at the same process, and, of course, since it changed also with an application or facilities, the good operating characteristic was acquired with no test equipment. Therefore, a ** form film which has a good operating characteristic with all test equipment was also desired strongly.

[0007]

[Problem(s) to be Solved by the Invention] The technical problem of this invention improves the fault of this conventional technique, and is to offer the advanced ** form film which has the shift tightness of ** in peel strength and a mold releasing layer though it ***** (ed), and the protection film for prepreps using it. Other technical problems of this invention are to give the outstanding inspection fitness over the online test equipment which used the light of all wavelength for the protection film for prepreps which used the above-mentioned ** form film and it further.

[0008]

[Means for Solving the Problem] this invention persons eliminated the silicone layer in which peel strength is first reduced extremely from the ** form film of an above-shown official report in order to solve an above-mentioned technical problem, and considered adopting the resin layer which is mainly concerned with thermosetting resin as a mold releasing layer. and the peel strength in the condition of having hardened thoroughly [thermosetting resin, such as a melamine,], for example although having 25mN(s) / peel strength of 5cm at least found out the desirable thing in order to have controlled exfoliation of the ** form film in the inside of the production process of prepreg as a result of this invention persons' examination -- at most -- it was 15mN(s) / 5cm, and in order to have controlled exfoliation of a ** form film, just abatement of a silicone layer was inadequate. By the way, the peel strength of thermosetting resin related to that hardening condition closely, and making the hardening condition of thermosetting resin imperfect also tried using this property. Consequently, although peel strength was able to be raised, since an unreacted functional group remained in a mold releasing layer, there was a problem of a mold releasing layer changing with the times of a path, or combining with the

front face of the product which the non-hardened part has protected firmly further, and carrying out condensation exfoliation from a ** form film. And in order to make hardening of a mold releasing layer into imperfection, it also became clear that the heat dimensional stability of the film obtained fell from making the temperature and time amount of heat treatment ease. From these viewpoints, it can be said that improvement in peel strength, shift prevention of a ** form agent, and heat dimensional stability have the relation of the rate rebellion of two.

[0009] Then, only by using a mold releasing layer as thermosetting resin, this invention persons thought that improvement in peel strength, shift prevention of a ** form agent, and the coexistence with heat dimensional stability were impossible, and tried research again from the presentation of the resin which constitutes a mold releasing layer. Consequently, header this invention was reached [that advanced peel strength can be given and], without making the condensation exfoliation of hardenability resin and the lowering of heat dimensional stability which constitute a mold releasing layer cause, when fibrin system resin is blended with hardenability resin.

[0010] In this way, according to this invention, it consists of fibrin system resin and hardenability resin, and it is the ** form film with which the mold releasing layer contain 85 to 15% of the weight was formed [latter / 15 - 85 % of the weight, and] in one field of polyester film in the former, the absolute values of the rate of a dimensional change at the time of carry out heating cooling in 170 degrees C from ordinary temperature under the stress of 0.785MPa are the shaping direction of polyester film, and a cross direction vertical to it, and they are the following formulas [0011], respectively.

$$\left[\frac{l_c - l_h}{l_h} \right] \leq 0.006$$

[0012] (-- a dimension [in / in l_c in the above-mentioned formula / 30 degrees C at the time of cooling] and l_h show the dimension in 30 degrees C at the time of heating.) -- it is provided for the ** form film characterized by being satisfied, and the protection film for preregs using it.

[0013]

[Embodiment of the Invention] The ** form film of this invention consists of fibrin system resin and hardenability resin, and consists of a mold releasing layer which contains 15 - 85 % of the weight, and the latter for the former 85 to 15% of the weight, and polyester film which has this mold releasing layer in one field. And the absolute values of the rate of a dimensional change at the time of carrying out heating cooling in 170 degrees C from ordinary temperature under the stress of 0.785MPa are the shaping direction (the direction of MD) of polyester film, and a cross direction (the direction of TD) vertical to it, and this ** form film needs to satisfy the following formulas, respectively.

$$\left[\frac{l_c - l_h}{l_h} \right] \leq 0.006$$

In addition, with the absolute value of the rate of a dimensional change here, insert the sample to which fixed tension is applied into the heating furnace of this equipment using a thermal stress distortion measuring device (SEIKO electronic incorporated company make, TMA/SS120C), and a heating furnace is heated from ordinary temperature. When sample temperature amounts to 170 degrees C, it is the absolute value of the value which broke the variation of tolerance which cooled the heating furnace to ordinary temperature, measured the dimension (l_h) in the sample temperature of 30 degrees C at the time of heating, and the dimension (l_c) in the sample temperature of 30 degrees C at the time of cooling, and deducted the former from the latter with the former dimension.

[0014] This invention is explained in full detail below in order of the polyester film used as the base, fibrin system resin, thermosetting resin, and a mold releasing layer.

It is desirable to use polyester film with good transparency for the polyester film which constitutes the ** form film of [polyester film] this invention, and especially the transparent polyester film by which

biaxial orientation was carried out is desirable. the crystalline line which serves as polyester which constitutes this polyester film from an aromatic series dibasic-acid component and a diol component -- it is saturated polyester, for example, polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene -2, 6-naphthalate, etc. are mentioned preferably. Polyethylene terephthalate, polyethylene -2, and 6-naphthalate are desirable especially from the field of workability in these. It is desirable to blend a non-subtlety particle, an organic particle, etc. with such polyester if needed as lubricant. As lubricant, a non-subtlety particle is desirable and especially an oxidation silicon particle is desirable. Moreover, amelioration agents other than lubricant can be combined with polyester, for example, sodium dodecylbenzenesulfonate etc. can be made to contain as an antistatic agent.

[0015] The polyester film in this invention can be manufactured by the manufacture approach learned from the former. For example, biaxial-stretching polyester film is fused with an extruder after drying the polyester used as a raw material, is extruded from dies (for example, T-die, I-die, etc.) to revolution cooling drum lifting, it is quenched, manufactures an unstretched film, subsequently to a lengthwise direction and a longitudinal direction extends this unstretched film, and can manufacture it by carrying out heat setting if needed. Moreover, in this invention, especially the thing for which heat relaxation processing which loosens to a lengthwise direction while heating under low tension after the above-mentioned heat setting processing is performed from a viewpoint which controls the dimensional change to the thermal stress of polyester film itself is desirable. The approach of maintaining 2 [14.7-98Ns / /] cm, and heat-treating the tension in the travelling direction of a film for 5 - 120 seconds at the temperature of 120-160 degrees C etc. is mentioned making the cross direction of a film contract the polyester film by which biaxial stretching was carried out at 1 - 10% as concrete heat relaxation processing. The thickness of polyester film has desirable 5-250 micrometers.

[0016] With the fibrin system resin as used in the field of [fibrin system resin] this invention, cellulose type resin is mentioned, for example, the inorganic acid or organic acid like a cellulose nitrate, cellulose acetate, a sulfuric-acid cellulose, or cellulose sodium xanthogenate, cellulose ester, methyl cellulose, ethyl cellulose, carboxyl methyl cellulose, cellulose acetyl butyrate, cellulose acetyl propionate, hydroxyethyl cellulose, or cellulose ether is mentioned. Since compatibility with the organic solvent used for the dissolution of thermosetting resin is high also in these, cellulose acetyl butyrate, cellulose acetyl propionate, and especially a cellulose nitrate are desirable.

[0017] Although it will not be limited especially if the hardenability resin as used in the field of [hardenability resin] this invention is resin hardened with light or electron rays, such as heat and ultraviolet rays, etc., it is desirable from effectiveness being for heat treatment at the time of at least one sort of thermosetting resin chosen from the group which consists of an epoxy resin, phenol resin, melamine resin, polyurethane resin, polyimide resin, and acrylic resin forming a mold releasing layer raising heat dimensional stability. Of course, although the resin hardened except heat, such as an acrylic photo-setting resin, may be used, it is necessary to perform independently the same heat treatment as the thermosetting resin other than hardening by the exposure of ultraviolet rays etc. in that case.

[0018] as the resin with which the greatest description of [mold releasing layer] this invention constitutes a mold releasing layer -- from fibrin system resin and hardenability resin -- becoming -- the former -- 15 - 85wt% and the latter -- 85 - 15wt% -- desirable -- 25 - 75wt% and the latter -- 75 - 25wt% -- especially -- desirable -- 30 - 70wt% and the latter -- 70 - 30wt% -- it is in having adopted what was blended. The percentage of fibrin system resin is less than 15%, or when the rate of hardenability ***** exceeded 85%, and hardening of hardenability resin takes time amount, a non-hardened material tends to remain and it changes into a perfect hardening condition, peel strength serves as imperfection. On the other hand, the junction force of the polyester film which the hardenability resin of a mold releasing layer carries out condensation exfoliation on the surface of a product, without peel strength's becoming it superfluously and strong that the rate of fibrin system resin exceeds 85wt(s)%, or the percentage of hardenability ***** is less than 15%, and separating with products, such as prepreg, in the case of exfoliation, and serves as the base, and a mold releasing layer becomes scarce, and it becomes easy to exfoliate from polyester film.

[0019] The mold releasing layer in this invention applies the coating liquid containing the above-

mentioned component to one side of polyester film, it heats, and dries and is formed. The approach learned as this method of application from the former, such as the bar coat method, a doctor blade method, the reverse roll coat method, or the gravure roll coat method, can be used. Desiccation and hardening of a paint film (heat curing, ultraviolet curing, etc.) can perform a respectively well-known approach individually or simultaneous. However, even when hardenability [as well as thermosetting resin / in addition to heat such as light, / in order to secure the heat dimensional stability of the ** type film obtained as it mentioned already] resin was used, after the paint film was applied, 160-200-degree C 140-210 degrees C are a 170-190-degree C temperature requirement especially preferably preferably, and it heat-treats in the tension range of 1.2-3.0MPa preferably 1.0 to 4.0 MPa. the absolute value of the rate of a dimensional change called for by said formula at the time of cooling to ordinary temperature by this heat treatment after heating from ordinary temperature to 170 degrees C under the stress of 0.785MPa -- the direction of MD, and the direction of TD -- respectively -- at most 0.6% -- ** -- the ** form film to say and which was extremely excellent in dimensional stability can be obtained. Although the absolute value of this rate of a dimensional change needs to be at most 0.6%, it is desirable that it is especially 0.45% at most at most 0.5%, and especially these make the range of 160-200 degrees C of heat treatment temperature 170-190 degrees C, and can attain the tension range by being especially referred to as 1.2-3.0MPa 1.1 to 3.5 MPa. Especially although especially the thickness of a paint film is not limited, the range of 0.5-2 micrometers is desirable 0.1-10 micrometers.

[0020] As mentioned above, although the ** form film of this invention which solves the 1st technical problem of this invention has been explained in full detail next, the coloring layer for giving the outstanding inspection fitness over the online test equipment which used the light of all wavelength further to the 2nd technical problem, i.e., the ** form film of said this invention, is explained in full detail below.

[0021] As for the field in which the mold releasing layer of polyester film was prepared in [coloring layer] this invention, it is desirable to prepare a coloring layer in a reverse field. A coloring layer is formed by applying the coating which mixed at homogeneity one or more sorts of coloring agents chosen from an inorganic pigment, an organic pigment, and a color to organic resin, and was distributed. From it being required to shade 400-800nm light to homogeneity, the black inorganic pigment of the coloring agent used for the coloring coatings of this invention is the most desirable. A carbon black metallurgy group oxide etc. is illustrated as such a black inorganic pigment.

[0022] The carbon black in this invention is carbon black holding relation of the chain structure whose mean diameter is 20-100nm. As carbon black, acetylene black, KETCHIEN black, and furnace black are mentioned by the difference in the manufacture approach. as acetylene black -- as the electrification acetylene black by DENKI KAGAKU KOGYO K.K., and KETCHIEN black -- as the Akzo Chemical KETCHIEN black EC, and KETCHIEN black EC-600DJ and furnace black -- the Cabot Corp. make -- Balkan Peninsula XC-72 etc. are mentioned. These carbon black may use together independent one sort or two sorts or more.

[0023] As a metallic oxide in this invention, the oxide of one which is chosen from four to 11 group and the metal group (Ti, V, Cr, Mn, Fe, Co, nickel, Cu) of the 4th period of metals [one sort of] is mentioned. Although these may be used independently, in order to make it function as a protection-from-light agent to the whole light field, it is desirable to use the multiple oxide which contains two or more sorts of metals from the above-mentioned metal group. The oxide which will not be limited especially if two or more sorts of metals are contained as a multiple oxide, for example, contains nickel-Cu, Cr-Fe, Fe-Cu, Cu-Cr, Fe-Co, Fe-Mn, Ti-Mn-Cu, Mn-Fe-Cu, Co-Fe-Cr, Cr-Mn-Cu, Cr-Cu-Fe, etc. is mentioned. A thing 1.0 micrometers or less has desirable mean particle diameter, and the above metallic oxides and a compound metallic oxide have an especially desirable thing 0.5 micrometers or less for improvement in membranous quality or a hue. Especially the configuration of this metallic-oxide particle may not be limited, but may be a globular shape, the shape of a Lynn piece, and an infinite form. Moreover, although there are also pigments other than yellow, red, blue, green, tea, and the black like gray in the inorganic pigment of the metallic oxide mentioned above or a compound metallic oxide, two or more sorts of these may be used, mixing them so that the whole region of a 400-900nm light field

may be shaded. Furthermore, an organic pigment and a color may mix two or more sorts similarly, and may make the whole region of a 400-900nm light field shade.

[0024] The various organic resin containing one or more sorts chosen from thermoplastics, hardenability resin, and fibrin system resin is used for the organic resin which constitutes the coloring layer in this invention. As thermoplastics, polyester resin, acrylic resin, polyvinyl system resin, phenoxy resin, etc. are mentioned, hardenability acrylic resin, melamine resin, an epoxy resin, urethane resin, etc. are mentioned as hardenability resin, and a nitrocellulose, an acetyl cellulose, etc. are mentioned as fibrin system resin. from fibrin system resin since the organic resin which constitutes a coloring layer also in these tends to double the dimensional change to thermal stress with the above-mentioned mold releasing layer, and hardenability resin -- becoming -- the former -- 15 - 85wt% and the latter -- 15 - 85wt% -- what is contained is desirable. In addition, the fibrin system resin used by the organic resin which constitutes a coloring layer, and hardenability resin are the same as that of what was stated by the above-mentioned mold releasing layer.

[0025] When making the coloring layer in this invention contain a coloring agent, the coating liquid containing an above-mentioned coloring agent and organic resin is applied to polyester film, and is formed. Coating liquid may be an organic solvent system, or may be a drainage system. Moreover, to coating liquid, a dispersant, a sedimentation inhibitor, a cross linking agent, a hardening accelerator catalyst, and since crawling etc. is not further produced on a film at the coating liquid of a drainage system, a surfactant etc. may be added suitably. The approach of adopting the approach of arbitration, for example, using as an approach of making coating liquid distributing a coloring agent, combining a ball mill, a roll mill, a stone mill, or a high-speed grinder, or the method of mixing said organic resin binder with what already distributed the coloring agent in the solvent and the dispersant is mentioned. Although the addition of the coloring agent of this invention changes with the class of coloring agent, or classes of the distributed approach and organic resin, its 1 - 50 % of the weight is desirable, and especially its 3 - 30 % of the weight is desirable. It is possible to form by the approach same as an approach of preparing a coloring layer as a mold releasing layer.

[0026] The total light transmission of the ** form film of this invention is 35 - 65% 25 to 75%, and, as for especially the coloring layer formed by the above-mentioned approach, it is desirable to prepare so that the deflection width of face of the permeability in a 400-900nm wavelength field may become **5%. It is recognized as the condition that there is no film depending on detection equipment when total light transmission exceeds 75%, it becomes impossible to identify, and it becomes impossible to detect the transmitted light to the equipment which will detect the transmitted light if total light transmission is 25% or less. Moreover, in case the deflection width of face of the permeability in a 400-900nm wavelength field is [only shading only especially the light of specific wavelength, and] two or more objects, for example, uses two or more detection equipments 5% or more for EPC, fault inspection, or printing pattern recognition, detection becomes impossible at a certain detection equipment which is using the different light source. In addition, since desiccation or the hardening process of this coloring layer also tends to control the dimensional change to the thermal stress of the ** form film obtained, it is [as well as the above-mentioned mold releasing layer] desirable to perform the same heat treatment as a mold releasing layer.

[0027]

[Example] Hereafter, this invention is explained in full detail according to an example. In addition, the physical-properties value and weighted solidity in this invention were measured by the following approach.

(1) Prepare the film of the shape of a strip of paper with a dimension rate-of-change width of face of 4mm as a sample, equip with this so that the distance between chucks may be set to 15mm to the fixture of a thermal stress distortion measuring device (SEIKO electronic incorporated company make, TMA/SS120C), and insert into the heating furnace of this equipment. And applying the fixed tension of 0.785MPa(s) to a sample, if heating furnace temperature is held and sample temperature becomes 170 degrees C until it carries out temperature up of the heating furnace from ordinary temperature to 200 degrees C with 200-degree-C programming rate for /and sample temperature becomes 170 degrees C at

200 degrees C, a heating furnace will be cooled to ordinary temperature with 200-degree-C cooling rate for /. Under the present circumstances, the dimension (lh) of a sample in case the sample temperature in a temperature-up process is 30 degrees C, and the dimension (lc) of a sample in case the sample temperature in a cooling process is 30 degrees C are measured, and let what broke the dimension which deducted the former from the latter with the former dimension be a rate of a dimensional change.

Therefore, the rate of a dimensional change is a negative value when it contracts with heating, and when it elongates with heating, it is shown by the forward value. In addition, this measurement was performed to the cross direction (the direction of TD) of polyester film respectively vertical to the shaping direction (the direction of MD) and the direction of MD of polyester film.

[0028] (2) Pass the laminator which was heated in the field of another side in polyester film unsettled to one field of peel strength glass epoxy prepreg (the Sumitomo Bakelite Co., Ltd. make, Sumi Wright ELC-4756), and was heated by superposition and 160 degrees C in the mold releasing layer side of a ** form film. And after this layered product became ordinary temperature, it judged to 5cm width of face, and the exfoliation force of a ** form film and prepreg was measured by part for 30mm/in tension rate with the tension tester.

[0029] (3) All the hazemeters made from light transmission Japan precision optics (JIS-K7105, standard source A) were used, the antistatic layer side was turned to the light source, and total light transmission was measured.

[0030] (4) Permeability fluctuation (fluctuation of the light transmission in each wavelength of 400-900nm)

Using the Shimadzu spectrophotometer (UV-3101PC), a 400-900nm transparency spectrum is measured at intervals of 1nm, the permeability in each wavelength is computed, and the permeability difference in each wavelength is computed by *(ing) with the value of the above-mentioned total light transmission. And the following criteria estimated.

O x which has all the permeability differences in :each wavelength in -5 - +5% of range : [0031] with the wavelength from which a permeability difference separates from -5 - +5% of range (5) as the detection fitness light source -- as the standard light A and C and the source of laser dispatch -- an argon laser (the product made from spectra FIJIKKU --) Wavelength : 514.5nm, ruby laser (made in Apollo, wavelength: 694nm), YAG laser excitation dye laser (conte NYUAMU, an adjustable wavelength region: 420-560nm (THG excitation)) The detection machine which used the lamp or laser of a total of six 550-740nm (SHG excitation) light sources or the source of dispatch is used. As a result of conducting fault inspection of the layered product which prepared the resin sheet on the ** form film, the case where O and at least one were not able to be inspected to which detection machine when inspection was possible was estimated as x.

[0032] In [example 1] o-chlorophenol, in 170 degrees C, the polyethylene terephthalate of the intrinsic viscosity 0.65 measured under 25-degree C temperature conditions was extruded through the slit-like die which was made to carry out melting after 3-hour desiccation, and was heated by 290 degrees C, was cast on the rotating drum, and the unstretched film was obtained. And where the obtained unstretched film is heated at 90 degrees C, it extended 3.7 times to the lengthwise direction, and it extended 3.8 times in the longitudinal direction in the condition of subsequently to 110 degrees C having heated, heat treatment (it contracts 5% to a cross direction) was carried out for 5 seconds at 235 degrees C, and the biaxial oriented film with a thickness of 25 micrometers was obtained.

[0033] Next, the cellulose-nitrate (die cel chemistry incorporated company make, FQRS 1/8) 50 section, The solid content which consists of the epoxy resin (oil-izing and Epicoat 1007 by shell epoxy incorporated company) 20 section, and the melamine resin (Hitachi, Inc. MERAN 13) 30 section the partially aromatic solvent of a methyl ethyl ketone / toluene / anone (50 sections / 40 sections / 10 section) -- criteria [weight / solution] -- carrying out -- 20wt(s)% -- it dissolved and the coating liquid for mold releasing layers which added the 3 sections of p-toluenesulfonic acid to the solid content 100 section as a hardening accelerator catalyst to this was prepared. And this coating liquid was applied to one field of said biaxial oriented film by the gravure coating machine so that it might become the coverage of 6 g/m2 on the basis of coating liquid weight, desiccation and hardening were performed for

1 minute at 190 degrees C, and the mold releasing layer with a thickness of 0.9 micrometers was prepared. In addition, all the film tension at the time of spreading of the coating liquid for mold releasing layers and heat treatment was 2.7MPa(s).

[0034] Subsequently, the copolymerized polyester resin 80 section (solid content it is the same as that of a ratio and the following), the methylol-ized melamine resin (Sumitomo Chemical Co., Ltd. make; SUMIMAL M-40W) 15 section, After mixing the surfactant (NS[by Nippon Oil & Fats Co., Ltd.]-208.5) 5 section and preparing in a water solution 20% of the weight, the carbon black water dispersing element (HMKmade from Country Coloring matter- # 7360) was added so that it might become 6.5% of the weight in a coloring layer as carbon black, and the coating liquid for coloring layers was created. And this coloring layer coating liquid was applied to the field of different another side from the field in which the mold releasing layer of polyester film was formed by the coverage of 7g/m² on the basis of paint volume, and heat treatment for 30 seconds was performed at 160 degrees C after that. The property of the obtained ** form film is shown in a table 1.

[0035] The same actuation as an example 1 was repeated except having changed the presentation of the solid content in the coating liquid for [example 2] mold releasing layers into the cellulose-nitrate (die cel chemistry incorporated company make, FQRS 1/8) 20 section, the epoxy resin (oil-izing and Epicoat 1007 by shell epoxy incorporated company) 40 section, and the melamine resin (Hitachi, Inc. MERAN 13) 40 section. The property of the obtained ** form film is shown in a table 1.

[0036] The same actuation as an example 1 was repeated except having changed the presentation of the solid content in the coating liquid for [example 3] mold releasing layers into the cellulose-nitrate (die cel chemistry incorporated company make, FQRS 1/8) 80 section and the melamine resin (Hitachi, Inc. MERAN 13) 20 section. The property of the obtained ** form film is shown in a table 1.

[0037] The same actuation as an example 1 was repeated except having changed the presentation of the solid content in the coating liquid for the [example 1 of comparison] mold releasing layers into the cellulose-nitrate (die cel chemistry incorporated company make, FQRS 1/8) 10 section, the epoxy resin (oil-izing and Epicoat 1007 by shell epoxy incorporated company) 50 section, and the melamine resin (Hitachi, Inc. MERAN 13) 40 section. The property of the obtained ** form film is shown in a table 1.

[0038] The same actuation as an example 1 was repeated except having changed the presentation of the solid content in the coating liquid for the [example 2 of comparison] mold releasing layers into the cellulose-nitrate (die cel chemistry incorporated company make, FQRS 1/8) 90 section and the melamine resin (Hitachi, Inc. MERAN 13) 10 section. The property of the obtained ** form film is shown in a table 1.

[0039] The same actuation as an example 1 was repeated except having transposed [example 4] polyethylene terephthalate to the polyethylene -2 of the intrinsic viscosity 0.62 measured in 25-degree C o-chlorophenol, and 6-naphthalate. The property of the obtained ** form film is shown in a table 1.

[0040] The same actuation as an example 1 was repeated except having changed the film tension at the time of performing heat treatment for 30 seconds in the [example 3 of comparison] 150 seconds into 5.0MPa. The property of the obtained ** form film is shown in a table 1.

[0041] The same actuation as the example 1 of a comparison was repeated except having not performed processing about formation of the coloring layer after forming the [example 4 of comparison] mold releasing layer. The property of the obtained ** form film is shown in a table 1.

[0042] The same actuation as an example 1 was repeated except having changed the addition of the carbon black in a [example 5] coloring layer to 10% of the weight. The property of the obtained ** form film is shown in a table 1.

[0043] The same actuation as an example 1 was repeated except having changed the addition of the carbon black in a [example 6] coloring layer to 3% of the weight. The property of the obtained ** form film is shown in a table 1.

[0044] The coating liquid for [example 7] coloring layers The copolymerized polyester resin (S pel 1510 by Hitachi Chemical Co., Ltd.) 70 section, In the melamine resin (Sanwa chemical NIKARAKKU NS-11) 30 section as a black inorganic pigment -- the pigment black 26 (a Fe-Cu-Mn multiple oxide --) C. I.77494 was prepared so that it might become 30% of concentration with the partially aromatic solvent

(ratios 1/1) of 12 *****, a methyl ethyl ketone, and toluene, this mixed solution was distributed so that the mean particle diameter of a pigment might be set to 0.5 micrometers using a Sand grinder mill (disperser), and coloring coating liquid was obtained. The solid content concentration of the obtained coating liquid is 25%, and repeated the same actuation as an example 1 except having changed p-toluenesulfonic acid into this coloring liquid to the resinous principle 100 section what added the 2.5 sections as a hardening accelerator catalyst. The property of the obtained ** form film is shown in a table 1.

[0045] The same actuation as an example 7 was repeated except having changed the addition of a [example 8] black inorganic pigment into the 25 sections. The property of the obtained ** form film is shown in a table 1.

[0046] The same actuation as an example 7 was repeated except having changed the addition of a [example 9] black inorganic pigment into the four sections. The property of the obtained ** form film is shown in a table 1.

[0047] the coloring liquid for [example 10] coloring layers -- a cellulose nitrate (die cel chemistry incorporated company make --) The FQRS1/8 44 section, the epoxy resin (oil-izing and Epicoat 1007 by shell epoxy incorporated company) 18 section, The solid content which consists of the black inorganic pigment (pigment black 26, C.I.77494) 12 section which consists of the melamine resin (Hitachi, Inc. MERAN 13) 26 section and a Fe-Cu-Mn multiple oxide Dissolve and this is received in p-toluenesulfonic acid as a hardening accelerator catalyst at the solid content 100 section. the partially aromatic solvent of a methyl ethyl ketone / toluene / anone (50 sections / 40 sections / 10 section) -- criteria [weight / solution] -- carrying out -- 20wt(s)% -- The same actuation as an example 1 was repeated except having changed into what carried out 3 section addition. The property of the obtained ** form film is shown in a table 1.

[0048]

[A table 1]

| | 寸法変化率 | | 剥離 強度 | 全光線 透過率 | 透過率 変動 | 検出 適正 |
|--------|-------|-------|----------|------------|-----------|----------|
| | T D方向 | M D方向 | | | | |
| | % | % | mN/5cm | % | ○ | ○ |
| 実施例 1 | -0.27 | 0.41 | 47 | 50 | ○ | ○ |
| 実施例 2 | -0.23 | 0.39 | 30 | 50 | ○ | ○ |
| 実施例 3 | -0.29 | 0.42 | 68 | 50 | ○ | ○ |
| 比較例 1 | -0.24 | 0.41 | 15 | 50 | ○ | ○ |
| 比較例 2 | -0.3 | 0.4 | 凝集剥離 | 50 | ○ | ○ |
| 実施例 4 | -0.12 | 0.18 | 33 | 50 | ○ | ○ |
| 比較例 3 | -0.73 | 0.57 | 30 | 50 | ○ | ○ |
| 比較例 4 | -0.29 | 0.4 | 15 | 89 | × | × |
| 実施例 5 | -0.33 | 0.4 | 46 | 28 | ○ | ○ |
| 実施例 6 | -0.25 | 0.42 | 46 | 74 | ○ | ○ |
| 実施例 7 | -0.3 | 0.43 | 44 | 52 | ○ | ○ |
| 実施例 8 | -0.35 | 0.4 | 44 | 74 | ○ | ○ |
| 実施例 9 | -0.28 | 0.42 | 44 | 28 | ○ | ○ |
| 実施例 10 | -0.32 | 0.38 | 40 | 49 | ○ | ○ |

[0049] A table 1 is considered below. The thing of the examples 1-10 illustrated as a ** form film of this invention also has the moderate adhesion to which peel strength exceeds 25mN(s) / 5cm, though it has the outstanding dimensional stability and the outstanding shift tightness of a ** form agent, peel strength exceeded 30mN(s) / 5cm, the content of fibrin system resin reached to an extreme, and especially 1/3 or more things were excellent in it. And since it was prepared in the field where the coloring layer which is a means to solve the 2nd technical problem of this invention also differs from the mold releasing layer of polyester film, detection fitness was also extremely excellent. Since the heat deformation by the side of a coloring layer and a mold releasing layer approximated especially the example 10 which a coloring layer becomes from hardenability resin and fibrin system resin like a mold releasing layer, it was the ** form

film excellent in smoothness with little curl.

[0050] these examples -- receiving -- the examples 1 and 4 of a comparison with few contents of fibrin system resin -- peel strength -- at most -- only 15mN(s) / 5cm, there was nothing, it is easy to exfoliate, and especially the example 4 of a comparison without a coloring layer was that in which detection fitness is also inferior. On the other hand, peel strength increased too much, and with it, since the junction force of polyester film and a mold releasing layer has become weaker conversely, exfoliation has generated the example 2 of a comparison superfluously added in fibrin system resin between polyester film and a mold releasing layer. Moreover, dimensional stability was scarce, a wrinkle and sag occurred and the example 3 of a comparison for which the tension at the time of heat treatment exceeded 4MPa(s) was deficient in peel strength compared with the example 1.

[0051]

[Effect of the Invention] Although thermosetting resin, such as silicone resin, fluororesin, resin that has a long-chain alkyl group, a melamine, and epoxy, a wax, or oil has been conventionally used as a ** form agent which constitutes a ** form film In using as protection films, such as prepreg Silicone resin and thermosetting resin have too low peel strength, and a protection film tends to exfoliate. Environmental destruction, the safety to the body, etc. to handling was difficult for fluororesin, and the resin which has a long-chain alkyl group was lacking in thermal resistance, and a wax and oil had the problem of being easy to shift to products, such as prepreg.

[0052] On the other hand, since the hardenability resin containing fibrin system resin is adopted as resin which constitutes a mold releasing layer according to the invention in this application, there is no problem in the safety to environmental destruction or the body, and though it has moderate peel strength, shift is prevented to products, such as prepreg of a mold releasing layer. Moreover, since it has the thermal resistance excellent in fibrin system resin and thermosetting resin, it can fully heat-treat and the extremely excellent ** form film which also has dimensional stability by setting film tension in this case to 4 or less MPas is offered.

[0053] And if the coloring layer illustrated by the invention in this application which can perform permeability fluctuation when irradiating a beam of light with a wavelength [each] of 400-900nm to the total light transmission of a ** form film 25 to 75% to -5 - 5% is prepared in the field of an opposite hand with a mold releasing layer, the ** form film excellent in the detection fitness in an inspection machine etc. and the protection film for prepregs using it will also be offered.

[Translation done.]